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Synthesis of the pentasaccharide repeating unit of the major *O*-antigen component from *Pseudomonas syringae* pv. *ribicola* NVPPB 1010

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Abstract—The synthesis of the repeating unit of the major *O*-antigen component from *Pseudomonas syringae* pv. *ribicola* NVPPB 1010 is reported. The strategy used was based on the successive coupling of a trisaccharide rhamnosyl trichloroacetimidate with a rhamnosyl acceptor with a free hydroxyl group on C-2. The pentasaccharide was then obtained by coupling with a *N*-Troc-tri-*O*-acetyl-glucosamine trichloroacetimidate. The synthesis allowed the oligomerisation of the repeating unit.

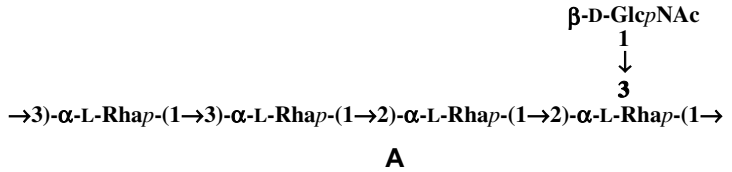
Keywords: *Pseudomonas ribicola*; O-chain; Glycosylation; Oligosaccharides; Repeating unit

1. Introduction

It has been recently reviewed[1] that O-chains of lipopolysaccharides (LPS) from phytopathogenic bacteria typically consist of repeating units composed of rhamnan backbones bearing single monosaccharide branches. Only a few types of sugars constitute these monosaccharide side chains, for example, GlcNAc.

Glucosaminylated rhamnans, that occur in human pathological bacteria, have been largely studied[2,3] and their repeating units have been synthesized.[4,5] They very often contain the GlcNAc residue as a component of the backbone structure, whereas the LPS from phytopathogenic bacteria very often present the GlcNAc unit as single monosaccharide side chain.

Since the role of the O-chain structures in phytopathogenic bacteria is much less known in comparison with the O-chain from human pathological bacteria, the synthesis of their repeating unit is strictly requested. Therefore, in order to investigate the structure–bioactivity relationship of the O-chain in plant infection, the synthesis of the glucosaminylated rhamnan repeating unit **A** (Scheme 1) of the phytopathogenic *P. syringae* pv. *ribicola* NVPPB 1010 bacterium, the causative agent



A

Scheme 1. Repeating unit of the major *O*-antigen component from *P. syringae* pv. *ribicola* NVPPB 1010.

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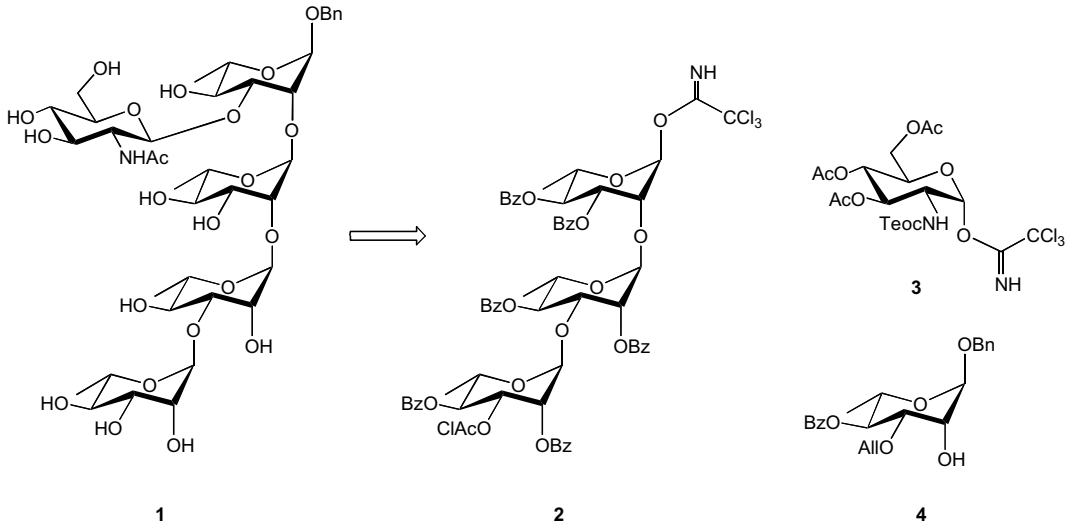


Scheme 2. Retrosynthetical analysis of structure **A**.

of defoliation of *Ribes aurum*,[7] is, at the best of our knowledge, for the first time reported.[†] The approach described in this paper aims at the synthesis of a pentasaccharide building block that can also be employed to obtain higher oligomers of the repeating unit **A**.

2. Results and discussion

As outlined in Scheme 1, the major repeating unit of the O-chain from *P. syringae* pv. *ribicola* NVPPB 1010 consists of a rhamnan backbone tetrasaccharide with a GlcNAc branch. This residue is attached to O-3 of a rhamnosyl residue, which is elongated by the rhamnosyl chain at C-2.

Retrosynthetic analysis of the benzylated pentasaccharide repeating unit **1** suggested a trisaccharide and a glucosaminyl donor and a rhamnosyl acceptor with a free OH group at C-2 and a selectively removable protecting group at C-3. We chose at best the building blocks **2**, **3**[9] and **4**, respectively (Scheme 2).

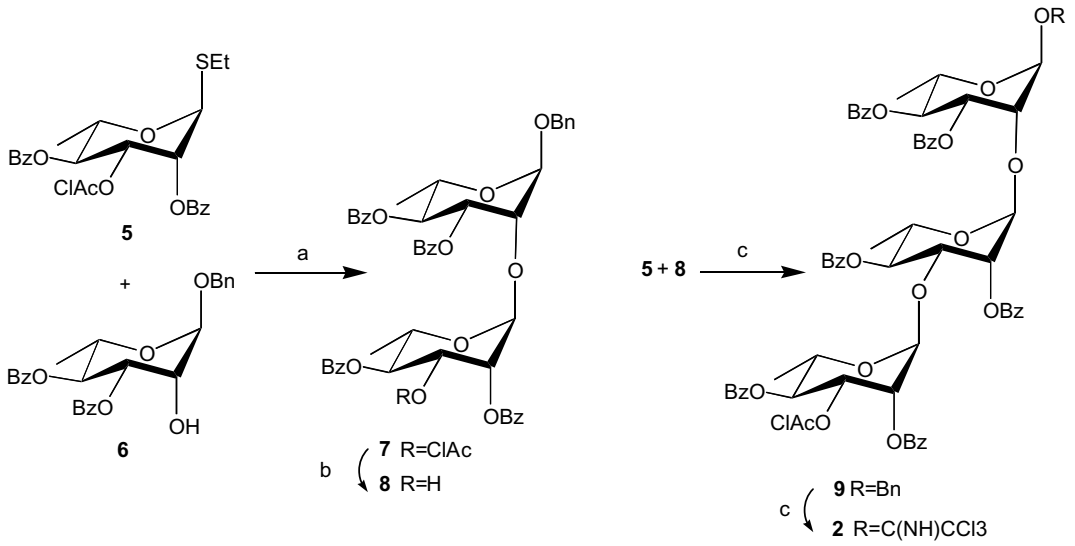
The synthesis of the trisaccharide donor **2** has been already reported in one of ours recent short communications.[10] It begins with the coupling of the thioglycoside **5**[10] and the acceptor **6**[11] following the typical conditions for the activation of disarmed thioglycoside with NIS/TfOH[12] (Scheme 3). The disaccharide **7** was obtained in high yield (82%). A selective removal of the chloroacetyl group on **7** with thiourea in ethanol (80% yield) afforded **8**, that, following the same activation condition used before, was then coupled with thioglycoside **5** obtaining the trisaccharide **9** in excellent yield (96%). Treating **9** with anhydrous $FeCl_3$ in CH_2Cl_2,[13] we could selectively cleave the benzyl protecting group on the anomeric position of **9**, obtaining a hemiacetal that was directly converted in the trisaccharide imidate **2** in an overall yield of 44% over two steps.

The rhamnosyl acceptor **4** was obtained by selective allylation of benzyl 4-*O*-benzoyl-α-L-rhamnopyranoside **10**,[10] whose α-anomeric configuration was assigned by low-field ^{1}H NMR chemical shift value (δ 5.191). The *cis*-diol **10** was activated as a stannylene acetal by refluxing with Bu_2SnO in 10:1 benzene–methanol. Subsequent alkylation with allyl bromide–Bu_4NBr in toluene gave the desired 3-allylated compound **4** in 85% yield (Scheme 4).

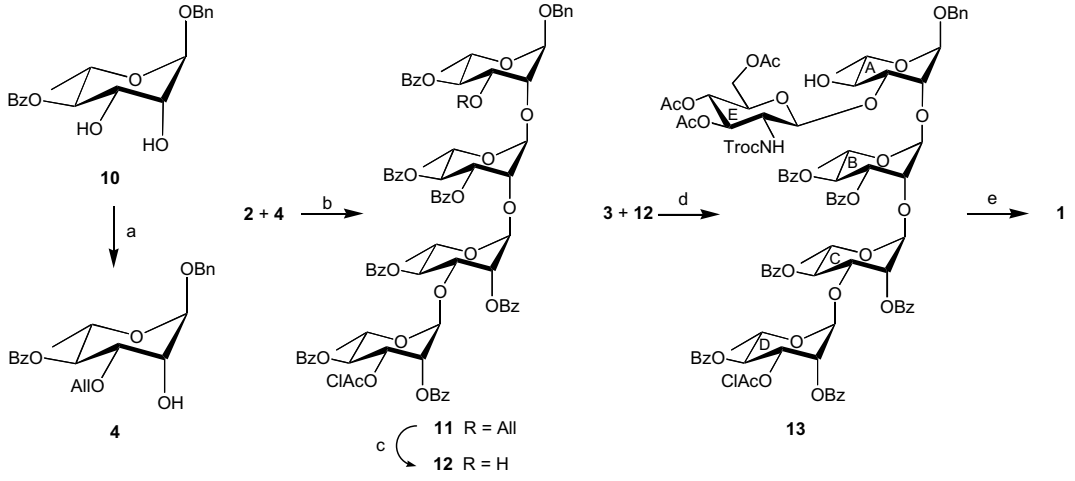
The tetrasaccharide **11** was obtained after coupling of the trisaccharide imidate **2** with the acceptor **4** in 79% yield. The α-configuration of the new glycosidic bond in **11** was ascertained by a coupled HMQC-COSY experiment ($J_{C\text{-}1',H\text{-}1'} = 173$ Hz). Subsequent deallylation of compound **11** with $PdCl_2$ in 5:2 methanol–dichloromethane furnished the tetrasaccharide acceptor **12** in 94% yield. Some dechloroacetylation of the starting material **11** was observed (5% detected by NMR and ESI-MS), however, this side reaction stopped after the initial phase. The following glycosylation of the tetrasaccharide **12** with the glucosaminyl donor **3**[9] afforded the pentasaccharide **13** in 45% yield together with a 51% recovery of unreacted **12**. The β-configuration of the new glycosidic bond was confirmed by a coupled HMQC-COSY experiment ($J_{C\text{-}1',H\text{-}1'} = 164$ Hz).

The final steps to the target molecule **1** required the deprotection of pentasaccharide **13**. The initial deprotection strategy was based on the conversion of the *N*-Troc group into an *N*-Ac group and a subsequent *O*-deacylation. Surprisingly the *N*-Troc/*N*-Ac conversion

[†] When this work was already completed we were acquainted with an alternative synthesis of our target, in a paper where a general method for the synthesis of glucosaminylated rhamnanic backbones was reported.[8]



Scheme 3. Reagents and conditions: (a) NIS, TfOH, molecular sieves 4 Å, CH_2Cl_2, −20 °C, 90 min; 82%; (b) NH_2CSNH_2, EtOH, rt, 16 h, 80%; (c) NIS, TfOH, molecular sieves 4 Å, CH_2Cl_2, −20 °C, 15 min; 96%; (d) i: anhydrous $FeCl_3$, CH_2Cl_2, rt, 45 min; ii: Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 80 min; 44% over two steps.



Scheme 4. Reagents and conditions: (a) i: Bu_2SnO, 10:1 benzene–methanol, reflux, 90 min; ii: AllBr, Bu_4NBr, toluene, 65 °C, 90 min; 85% over two steps; (b) $BF_3{\cdot}OEt_2$, molecular sieves 4 Å, CH_2Cl_2, −50 °C, 30 min; 79%; (c) $PdCl_2$, 5:2 methanol–dichloromethane, rt, 4 h; 94%; (d) TMSOTf, molecular sieves 4 Å, CH_2Cl_2, −10 °C, 3 h; 45%; (e) i: 2 M KOH, THF, 40 °C, 19 h; ii: Ac_2O, MeOH, rt, 2 h; 56% over two steps.

with Zn/Ac_2O[9] was ineffective with the pentasaccharide **13**. Thus, a different deprotection strategy was envisioned starting with the complete removal of all ester groups and the subsequent replacement of the Troc moiety by an *N*-acetyl group. This approach was also not successful because the *N*-Troc function was converted to a methyl carbamate during methanolysis with NaOMe in MeOH. Finally, treatment of **13** with 2 M KOH in THF assured global deacylation and basic removal of the Troc moiety. The free amino group of the intermediate pentasaccharide was selectively acetylated with Ac_2O in MeOH to obtain the desired repeating unit **1**. In Table 1 the ^1H and ^{13}C NMR chemical shifts for the synthetic pentasaccharide **1** and the natural O-chain[6] show very good accordance, except for few values; in particular the ^{13}C NMR $C\text{-}3^D$ signal is shifted highfield (8.2 ppm) in comparison with the value of the natural O-chain, due to the absence of the glycosylation shift for our oligosaccharide structure. There are other differences related to some ^1H and ^{13}C NMR values of the residue A, due to the effect of the benzyl group as a glycon.

In conclusion, we have synthesized a rhamnanic pentasaccharide containing a GlcNAc branch corresponding to the major O-chain repeating unit from *P. syringae* pv. *ribicola* NVPPB 1010. It is noteworthy that

Table 1. ^{1}H and ^{13}C NMR chemical shifts (δ in ppm) of **1** (in parentheses the differences in ppm between **1** and the related natural O-polysaccharide[6] are given)

Sugar residue	H-1	H-2	H-3	H-4	H-5	H-6	H-6′
A	4.83	4.13	3.84	3.51	3.70	1.27	
	(−0.27)	(−0.18)	(−0.13)	(−0.03)	(−0.14)	(−0.04)	
B	5.26	4.02	3.85	3.45	3.52	1.13	
	(−0.07)	(−0.04)	(−0.05)	(−0.04)	(−0.17)	(−0.15)	
C	4.95	4.13	3.86	3.53	3.79	1.23	
	(−0.11)	(−0.01)	(0.01)	(−0.06)	(−0.01)	(−0.11)	
D	5.06	4.25	4.07	3.47	3.84	1.29	
	(−0.01)	(0.10)	(0.16)	(−0.12)	(−0.03)	(−0.03)	
E	4.68	3.71	3.53	3.39	3.39	3.71	3.88
	(−0.07)	(−0.03)	(−0.05)	(−0.03)	(−0.06)	(−0.04)	(−0.06)
	C-1	C-2	C-3	C-4	C-5	C-6	
A	98.5	77.6	81.5	69.9	70.3	18.0	
	(−3.6)	(0.3)	(0.01)	(−2.5)	(0.3)	(0.2)	
B	100.7	79.2	70.9	73.3	70.6	17.9	
	(−0.1)	(0.1)	(−0.4)	(−0.4)	(0.1)	(−0.1)	
C	102.8	71.1	78.9	72.4	70.3	18.0	
	(0.2)	(−0.2)	(−0.2)	(−0.4)	(0.3)	(−0.4)	
D	103.0	71.5	71.4	70.6	70.9	18.0	
	(−0.1)	(0.2)	(−8.2)	(−2.1)	(0.3)	(0.1)	
E	104.5	56.6	75.3	71.0	76.7	62.1	
	(0.4)	(−0.7)	(−0.1)	(−0.7)	(−0.3)	(−0.6)	

the synthetic approach used should also permit the anomeric activation of the repeating unit to obtain higher oligomers suitable for structure–activity studies.

3. Experimental

3.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 NMR (400 MHz) and Bruker Avance-360 NMR (360 MHz) in DMSO-d_6 (internal standard, for ^{1}H: $(CH_3)_2SO$ at δ 2.49; for ^{13}C: $(CH_3)_2SO$ at δ 39.5), in $CDCl_3$ (internal standard, for ^{1}H: $CHCl_3$ at δ 7.26; for ^{13}C: $CDCl_3$ at δ 77.0) and in D_2O (internal standard, for ^{1}H: $(CH_3)_2CO$ at δ 2.22; for ^{13}C: $(CH_3)_2CO$ at δ 31.5, respectively). Assignment of proton and carbon chemical shifts were based on DQF-COSY, TOCSY, ROESY, HSQC and HMQC-COSY experiments. Positive ESI-MS spectra were recorded on a Finnigan LCQ-DECA ion trap mass spectrometer. Optical rotations were measured on a JASCO P-1010 polarimeter. Elementary analysis were performed on a Carlo Erba 1108 instrument. Analytical thin layer chromatography (TLC) was performed on aluminium plates precoated with Merck Silica Gel 60 F_{254} as the adsorbent. The plates were developed with 5% H_2SO_4 ethanolic solution and then heated to 130 °C. Column chromatography was performed on Kieselgel 60 (63–200 mesh). Gel filtration chromatography were performed on a Biogel P2 column (1.0×20 cm) with H_2O as eluant.

3.2. Benzyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (7)

To a stirred solution of thioglycoside **5**[9] (1.658 g, 3.37 mmol), acceptor **6**[10] (1.208 g, 2.61 mmol) and NIS (1.665 g, 7.41 mmol) in CH_2Cl_2 (50 mL) containing powdered 4 Å molecular sieves, at −20 °C was added TfOH (130 μL, 1.50 mmol) and the mixture was stirred until TLC showed that the reaction was complete (90 min). The brown solution was then filtered on Celite; the filtrate was diluted with CH_2Cl_2 (150 mL) and then extracted with $Na_2S_2O_3$ 10% (200 mL), and then with $KHCO_3$ 2 M (200 mL). The organic phase was dried and concentrated. Silica gel chromatography (14:1 cyclohexane–ethyl acetate) of the residue afforded **7** (1.915 g, 82%) as a white foam. $[\alpha]_D$ +79.4 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO-d_6): δ 7.99–7.30 (m, 25H, 5Ph), 5.686 (dd, $J_{3,4} = 9.8$ Hz, $J_{3,2} = 3.0$ Hz, 1H, H-3^{A}), 5.672 (br s, 1H, H-2^{B}), 5.606 (dd, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 3.3$ Hz, 1H, H-3^{B}), 5.441 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^{A}), 5.360 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1H, H-4^{B}), 5.285 (br s, 1H, H-1^{B}), 5.121 (br s, 1H, H-1^{A}), 4.813 (d, $J_{gem} = 11.9$ Hz, 1H, OC$H_2\Phi$), 4.665 (d, $J_{gem} = 11.9$ Hz, 1H, OC$H_2\Phi$), 4.407 (br s, 1H, H-2^{A}), 4.236 (d, $J_{gem} = 15.2$ Hz, 1H, CH_2Cl), 4.11–4.21 (m, 3H, CH_2Cl, H-5^{A}, H-5^{B}), 1.261 (d, $J_{6,5} = 6.2$ Hz, 3H, H-6^{A}), 1.131 (d, $J_{6,5} = 6.1$ Hz, 3H, H-6^{B}). ^{13}C NMR (90 MHz, DMSO-d_6): δ 166.8–164.7 (5C, 5*C*=O), 137.1–127.9 (C–Ar), 98.1 (1C, C-1^{A}), 97.0 (1C, $^{1}J_{C,H} = 173$ Hz, C-1^{B}), 75.8 (1C, C-2^{A}), 71.9 (1C, C-4^{A}), 70.8 (1C, C-4^{B}), 70.4 (1C, C-3^{B}), 70.2 (1C, C-3^{A}), 69.6 (1C, C-2^{B}), 68.8 (1C, OC$H_2\Phi$), 66.8 (1C, C-5^{B}), 66.2 (1C,

C-5^{A}), 40.7 (1C, CH$_2$Cl), 17.6 (1C, C-6^{A}), 17.2 (1C, C-6^{B}). ESI-MS for $C_{49}H_{45}ClO_{14}$ (m/z): M_r (calcd) 892.2, M_r (found) 915.1 (M+Na)$^+$. Anal. calcd: C, 65.88; H, 5.08. Found: C, 66.01; H, 5.03.

3.3. Benzyl (2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (8)

A solution of **7** (1.860 g, 2,08 mmol) and thiourea (1.425 g, 18.72 mmol) in absolute EtOH (45 mL) was stirred at 25 °C until TLC showed that the reaction was complete (16 h). The solution was then concentrated and the residue was triturated with CH_2Cl_2 (150 mL) and then filtrated. The filtrate was extracted firstly with HCl 1 N (150 mL), then with $KHCO_3$ 2 M (150 mL) and finally with water (150 mL). The organic phase was dried and concentrated. Silica gel chromatography (11:1 cyclohexane–ethyl acetate) of the residue afforded **8** (1.367 g, 80%) as a white foam. $[\alpha]_D$ +39 (c 0.3, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO-d_6): δ 8.03–7.30 (m, 25H, 5Ph), 5.711 (d, $J_{H,OH} = 5.6$ Hz, 1H, OH-3^{B}), 5.679 (dd, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 3.0$ Hz, 1H, H-3^{A}), 5.525 (br s, 1H, H-2^{B}), 5.423 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1H, H-4^{A}), 5.184 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^{B}), 5.130 (br s, 1H, H-1^{B}), 5.033 (br s, 1H, H-1^{A}), 4.807 (d, $J_{gem} = 11.9$ Hz, 1H, OC$H_2\Phi$), 4.659 (d, $J_{gem} = 11.9$ Hz, 1H, OC$H_2\Phi$), 4.357 (br s, 1H, H-2^{A}), 4.240 (m, 1H, H-3^{B}), 4.128 (m, 1H, H-5^{A}), 4.016 (m, 1H, H-5^{B}), 1.255 (d, $J_{6,5} = 6.1$ Hz, 3H, H-6^{A}), 1.067 (d, $J_{6,5} = 6.1$ Hz, 3H, H-6^{B}). ^{13}C NMR (90 MHz, DMSO-d_6): δ 166.8–164.7 (4C, C=O), 137.0–128.0 (C–Ar), 98.8 (1C, C-1^{B}), 97.2 (1C, C-1^{A}), 75.8 (1C, C-2^{A}), 74.2 (1C, C-4^{B}), 72.6 (1C, C-2^{B}), 72.0 (1C, C-4^{A}), 70.6 (1C, C-3^{A}), 68.8 (1C, O–CH$_2\Phi$), 66.9 (1C, C-5^{B}), 66.4 (1C, C-3^{B}), 66.3 (1C, C-5^{A}), 17.7 (1C, C-6^{A}), 17.4 (1C, C-6^{B}). ESI-MS for $C_{47}H_{44}O_{13}$ (m/z): M_r (calcd) 816.3, M_r (found) 839.3 (M+Na)$^+$. Anal. calcd: C, 69.11; H, 5.43. Found: C, 69.00; H, 5.45.

3.4. Benzyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (9)

A stirred solution of thioglycoside **5**[9] (1.033 g, 2.10 mmol), acceptor **8** (1.318 g, 1.61 mmol) and NIS (1.039 g, 4.62 mmol) in CH_2Cl_2 (45 mL) containing freshly powdered 4 Å molecular sieves, was cooled at −20 °C. TfOH (80 μL, 0.92 mmol) was added and the mixture was stirred until TLC (3:1 cyclohexane–ethyl acetate) showed that the reaction was complete (15 min). The brown solution was then filtered on Celite, the filtrate diluted with CH_2Cl_2 (150 mL) and then extracted with $Na_2S_2O_3$ 10% (200 mL) and then with $KHCO_3$ 2 M (200 mL). The organic phase was dried and concentrated. Silica gel chromatography (25:2 cyclohexane–ethyl acetate) of the residue afforded **9** (1.921 g, 96%) as a white foam. $[\alpha]_D$ +120.8 (c 1.9, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO-d_6): δ 8.07–7.33 (m, 35H, 7Ph), 5.676 (dd, $J_{3,4} = 10.0$ Hz, $J_{3,2} = 3.0$ Hz, 1H, H-3^{A}), 5.662 (br s, 1H, H-2^{B}), 5.441 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1H, H-4^{A}), 5.376 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1H, H-4^{B}), 5.337 (s, 1H, H-1^{C}), 5.309 (s, 1H, H-1^{B}), 5.274 (dd, $J_{3,4} = 10.1$ Hz, $J_{3,2} = 3.1$ Hz, 1H, H-3^{C}), 5.216 (t, $J_{4,5} = J_{4,3} = 9.9$ Hz, 1H, H-4^{C}), 5.077 (br s, 1H, H-2^{C}), 5.054 (s, 1H, H-1^{A}), 4.806 (d, $J_{gem} = 11.9$ Hz, 1H, OC$H_2\Phi$), 4.655 (bd, 2H, OC$H_2\Phi$, H-3^{B}), 4.409 (br s, 1H, H-2^{A}), 4.144 (m, 3H, H-5^{A}, H-5^{B}, H-5^{C}), $\delta = 4.069$ (d, $J_{gem} = 15.1$ Hz, 1H, CH_2Cl), $\delta = 3.995$ (d, $J_{gem} = 15.1$ Hz, 1H, CH_2Cl), $\delta = 1.248$ (d, $J_{6,5} = 6.2$ Hz, 3H, H-6^{A}), $\delta = 1.131$ (t, 6H, H-6^{B}, H-6^{C}). ^{13}C NMR (90 MHz, DMSO-d_6): δ 166.4–164.3 (7C, C=O), 137.0–127.9 (C–Ar), 98.6 (1C, C-1^{B}), 98.1 (1C, C-1^{C}, $^1J_{C,H} = 176.1$ Hz), 97.1 (1C, C-1^{A}), 76.5 (1C, C-2^{A}), 73.8 (1C, C-3^{B}), 72.9 (1C, C-4^{B}), 72.0 (1C, C-4^{A}), 71.7 (1C, C-2^{B}), 70.8 (1C, C-4^{C}), 70.5 (1C, C-3^{A}), 69.8 (1C, C-3^{C}), 69.5 (1C, C-2^{C}), 68.8 (1C, OC$H_2\Phi$), 66.8 (2C, C-5^{B}, C-5^{C}), 66.3 (1C, C-5^{A}), 40.6 (1C, CH$_2$Cl), 17.6 (1C, C-6^{A}), 17.2 (2C, C-6^{B}, C-6^{C}). ESI-MS for $C_{69}H_{63}ClO_{20}$ (m/z): M_r (calcd) 1246.4, M_r (found) 1269.3 (M+Na)$^+$. Anal. calcd: C, 66.42; H, 5.09. Found: C, 66.54; H, 4.88.

3.5. (2,4-Di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (2)

To a solution of **9** (730 mg, 0.585 mmol) in CH_2Cl_2 (50 mL) was added anhydrous $FeCl_3$ (2.2 g, 13.6 mmol) and the green mixture so obtained was stirred at room temperature. When TLC (2:1 cyclohexane–ethyl acetate) showed complete conversion of **9** in a new product (45 min), CH_2Cl_2 was added (750 mL) and the solution was extracted with water (750 mL) and then with $KHCO_3$ 2 M (750 mL). The organic phase was dried and concentrated. Silica gel chromatography (9:2 cyclohexane–ethyl acetate) of the residue afforded an amorphous solid (352 mg, hemiacetal) that was solved in freshly distilled CH_2Cl_2 (6 mL). To the solution cooled at 0 °C were added Cl_3CCN (115 μL, 1.15 mmol) and DBU (14 μL, 0.11 mmol). When TLC (2:1 cyclohexane–ethyl acetate) showed that the reaction was completed (80 min), the solution was concentrated at 20 °C. Silica gel chromatography (12:1 cyclohexane–ethyl acetate) of the residue afforded **2** (335 mg, 44%) as a white foam. $[\alpha]_D$ +120.8 (c 1.5, CH_2Cl_2); ^{1}H NMR (360 MHz, DMSO-d_6): δ 8.10–7.35 (m, 30H, 6Ph), 6.414 (s, 1H, H-1^{A}), 5.738 (d, $J_{3,4} = 9.6$ Hz, 1H, H-3^{A}), 5.658 (br s, 1H, H-2^{B}), 5.549 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^{A}), 5.414 (t, 3H, H-4^{B}, H-1^{C}, H-1^{B}), 5.271 (dd, $J_{3,4} = 10.1$ Hz, $J_{3,2} = 2.6$ Hz, 1H, H-3^{C}), 5.208 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^{C}), 5.083 (br s, 1H, H-2^{C}), 4.731 (d, $J_{3,4} = 9.7$ Hz, 1H, H-3^{B}), 4.653 (br s, 1H, H-2^{A}), 4.277

(m, 2H, H-5^A, H-5^B), 4.160 (m, 1H, H-5^C), 4.070 (d, J_{gem} = 15.1 Hz, 1H, CH_2Cl), 3.998 (d, J_{gem} = 15.1 Hz, 1H, OCH_2Cl), 1.283 (t, 6H, H-6^A, H-6^B), 1.127 (d, $J_{6,5}$ = 6.2 Hz, 3H, H-6^C). ^{13}C NMR (90 MHz, DMSO-d_6): δ 166.4–164.2 (7C, *C*=O), 157.3 (1C, *C*=NH), 134.1–128.6 (C–Ar), 98.2 (2C, C-1^B, C-1^C), 95.0 (1C, $^1J_{C,H}$ = 179 Hz, C-1^A), 74.4 (C-2^A), 73.9 (C-3^B), 72.6 (C-4^B), 71.6 (C-2^B), 71.1 (C-4^A), 70.7 (C-4^C), 70.0 (C-3^A), 69.7 (C-3^C), 69.3 (C-2^C), 68.9 (C-5^A), 67.0 (C-5^B), 66.8 (C-5^C), 40.5 (O*C*H$_2$Cl), 17.4 (C-6^A, C-6^B), 17.0 (C-6^C). ESI-MS for $C_{64}H_{57}Cl_4NO_{20}$ (m/z): M_r (calcd) 1299.2, M_r (found) 1322.3 (M+Na)$^+$. Anal. calcd: C, 59.04; H, 4.41; N, 1.08. Found: C, 59.54; H, 4.55; N, 1.07.

3.6. Benzyl 3-*O*-allyl-4-*O*-benzoyl-α-L-rhamnopyranoside (4)

To a solution of **10**[9] (252 mg, 0.703 mmol) in 10:1 benzene–methanol (5 mL), Bu_2SnO (215 mg, 0.861 mmol) was added and the mixture was stirred at reflux for 90 min, until the Bu_2SnO was completely dissolved. The mixture was dried in vacuo, and the white foamy residue was dissolved in toluene (2.5 mL). Bu_4NBr (230 mg, 0.714 mmol) and subsequently AllBr (610 μL, 7.4 mmol) were added and the solution was stirred at 65 °C. When the TLC (2:1 cyclohexane–ethyl acetate) showed that all the starting material **10** was consumed (90 min), the solution was dried in vacuo. Silica gel chromatography (6:1 petroleum ether–ethyl acetate) of the residue afforded **4** (237 mg, 85%) as a white foam: $[\alpha]_D$ −33.8 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.09–7.30 (m, 10 H, 2Ph), 5.82–5.64 (m, 1H, C*H*=CH$_2$), 5.311 (t, 1H, $J_{4,5}$ = $J_{4,3}$ = 9.7 Hz, H-4), 5.160 (dd, 1H, J_{vic} = 17.2 Hz, J_{gem} = 1.6 Hz, CH=CH_2 *trans*), 5.063 (dd, 1H, J_{vic} = 10.2 Hz, J_{gem} = 1.4 Hz, CH=CH_2 *cis*), 4.987 (br s, 1H, H-1), 4.757 (d, 1H, J_{gem} = 12.0 Hz, OCH_2Ph), 4.556 (d, 1H, J_{gem} = 12.0 Hz, OCH_2Ph), 4.16–3.84 (m, 5H, H-2, H-3, H-5, OCH_2CH=CH$_2$), 1.255 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ165.7 (1C, *C*OPh), 134.2–128.0 (C–Ar), 133.1 (1C, *C*H=CH$_2$), 117.5 (1C, CH=*C*H$_2$), 98.4 (1C, C-1), 76.8 (1C, C-3), 73.2 (1C, C-4), 71.0 (1C, C-2), 69.3 (1C, O*C*H$_2$CH=CH$_2$), 68.8 (1C, O*C*H$_2$Ph), 66.5 (1C, C-5), 17.4 (1C, C-6). ESI-MS for $C_{23}H_{26}O_6$ (m/z): M_r (calcd) 398.2, M_r (found) 421.0 (M+Na)$^+$. Anal. calcd: C, 69.33; H, 6.58. Found: C, 69.55; H, 6.56.

3.7. Benzyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3-*O*-allyl-4-*O*-benzoyl-α-L-rhamnopyranoside (11)

A mixture of imidate **2** (352 mg, 0.271 mmol), acceptor **4** (77 mg, 0.194 mmol) and freshly powdered 4 Å molecular sieves was suspended in absolute CH_2Cl_2 (9 mL). The mixture was stirred at −50 °C and after 30 min BF_3·OEt_2 (34 μL, 0.271 mmol) was added. When TLC (2:1 cyclohexane–ethyl acetate) showed that the reaction was complete (30 min), the mixture was diluted with CH_2Cl_2 (10 mL), filtered over Celite, and the filtrate extracted with $NaHCO_3$ 1 M. The organic layer was collected, dried, and concentrated. The residue was purified by silica gel chromatography (6:1 petroleum ether–ethyl acetate) to give tetrasaccharide **11** (237 mg, 79%) as a white foam: $[\alpha]_D$ +88.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–7.23 (m, 40H, 8Ph), 5.837 (dd, 1H, $J_{3,4}$ 9.7 Hz, $J_{3,2}$ 3.2 Hz, H-3^B), 5.76–5.66 (m, 1H, C*H*=CH$_2$), 5.717 (br s, 1H, H-2^C), 5.552 (t, 1H, $J_{4,5}$ = $J_{4,3}$ 9.7 Hz, H-4^B), 5.544 (t, 1H, $J_{4,5}$ = $J_{4,3}$ 9.7 Hz, H-4^C), 5.439 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{3,2}$ 3.3 Hz, H-3^D), 5.382 (t, 1H, $J_{4,5}$ = $J_{4,3}$ 9.7 Hz, H-4^A), 5.366 (br s, 1H, H-1^B), 5.323 (t, 1H, $J_{4,5}$ = $J_{4,3}$ 9.6 Hz, H-4^D), 5.236 (br s, 1H, H-1^C), 5.200 (br s, 1H, H-1^D), 5.183 (br s, 1H, H-2^D), 5.108 (dd, 1H, J_{vic} 17.6 Hz, J_{gem} 1.6 Hz, CH=CH_2 *trans*), 4.944 (br s, 1H, H-1^A), 4.935 (dd, 1H, J_{vic} 9.9 Hz, J_{gem} 1.6 Hz, CH=CH_2 *cis*), 4.793 (d, 1H, J_{gem} 12.2 Hz, OCH_2Ph), 4.596 (d, 1H, J_{gem} 12.2 Hz, OCH_2Ph), 4.588 (dd, 1H, $J_{3,4}$ 9.7 Hz, $J_{3,2}$ 3.3 Hz, H-3^C), 4.500 (br s, 1H, H-2^B), 4.25–4.18 (m, 2H, H-2^A, H-5^D), 4.17–4.03 (m, 3H, H-5^B, H-5^C, OCH_2CH=CH$_2$), 4.01–3.95 (m, 3H, H-3^A, H-5^A, OCH_2CH=CH$_2$), 3.730 (d, 1H, J_{gem} 14.9 Hz, COCH_2Cl), 3.682 (d, 1H, J_{gem} 14.9 Hz, COCH_2Cl), 1.304 (d, 3H, $J_{6,5}$ 6.4 Hz, H-6^A), 1.286 (d, 3H, $J_{6,5}$ 6.4 Hz, H-6^C), 1.228 (d, 3H, $J_{6,5}$ 6.4 Hz, H-6^B), 1.200 (d, 3H, $J_{6,5}$ 6.4 Hz, H-6^D); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1 (1C, *C*OCH$_2$Cl), 165.3–164.6 (7C, *C*OPh), 134.1 (1C, CH$_2$C*H*=CH$_2$), 133.7–127.5 (C–Ar), 117.1 (1C, CH$_2$CH=CH_2), 99.9 (1C, $J_{C,H}$ 173 Hz, C-1^B), 98.7 (1C, C-1^C), 98.6 (1C, C-1^D, $^1J_{C,H}$ = 173 Hz), 97.8 (1C, C-1^A), 77.0 (1C, C-3^A), 75.8 (1C, C-2^B), 74.6 (1C, C-3^C), 74.3 (1C, C-2^A), 73.3 (1C, C-4^A), 73.2 (1C, C-4^C), 71.9 (1C, C-4^B), 71.8 (1C, C-5^B), 71.6 (2C, C-2^C, C-5^A), 71.1 (1C, C-4^D), 70.3 (1C, C-3^B), 70.2 (1C, C-3^D), 69.7 (1C, C-2^D), 68.8 (1C, O*C*H$_2$Ph), 67.4 (2C, C-5^C, C-5^D), 67.0 (1C, CH_2CH=CH$_2$), 40.0 (1C, CO*C*H$_2$Cl), 18.7–18.4 (4C, C-6^A, C-6^B, C-6^C, C-6^D). ESI-MS for $C_{85}H_{81}ClO_{25}$ (m/z): M_r (calcd) 1536.5, M_r (found) 1559.6 (M+Na)$^+$. Anal. calcd: C, 66.38; H, 5.31. Found: C, 66.60; H, 5.27.

3.8. Benzyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-4-*O*-benzoyl-α-L-rhamnopyranoside (12)

To a solution of tetrasaccharide **11** (115 mg, 0.075 mmol) in 5:2 methanol–dichloromethane, anhydrous $PdCl_2$ (1.3 mg, 7.5 μmol) was added and the mixture was stirred at room temperature until TLC (2:1 cyclohexane–ethyl acetate) indicated (4 h) that the starting material was consumed. The mixture was fil-

tered over Celite diluted with dichloromethane (50 mL) and extracted with saturated NaCl solution (50 mL). The organic layer was collected and dried. Silica gel chromatography (11:2 cyclohexane–ethyl acetate) of the residue afforded **12** (105 mg, 94%) as a white foam. $[\alpha]_D$ +80.2 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 8.16–7.23 (m, 40H, 8Ph), 5.795 (dd, 1H, $J_{3,4} = 9.7$ Hz, $J_{3,2} = 3.3$ Hz, H-3^B), 5.697 (br s, 1H, H-2^C), 5.569 (t, 1H, $J_{4,3} = J_{4,5} = 9.7$ Hz, H-4^B), 5.556 (t, 1H, $J_{4,3} = J_{4,5} = 9.8$ Hz, H-4^C), 5.437 (dd, 1H, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 3.2$ Hz, H-3^D), 5.325 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^D), 5.279 (br s, 1H, H-1^B), 5.215 (br s, 1H, H-1^C), 5.197 (br s, 1H, H-1^D), 5.185 (br s, 1H, H-2^D), 5.138 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4^A), 5.003 (br s, 1H, H-1^A), 4.789 (d, 1H, $J_{gem} = 12.2$ Hz, OCH_2Ph), 4.593 (d, 1H, $J_{gem} = 12.2$ Hz), 4.552 (dd, 1H, $J_{3,4} = 9.8$ Hz, $J_{3,2} = 3.3$ Hz, H-3^C), 4.493 (br s, 1H, H-2^B), 4.23–4.12 (m, 4H, H-5^A, H-5^B, H-5^C, H-5^D), 4.115 (br s, 1H, H-2^A), 4.052 (dd, $J_{3,4} = 9.6$ Hz, $J_{3,2} = 3.2$ Hz, H-3^A), 3.728 (d, 1H, $J_{gem} = 14.6$ Hz, COCH_2Cl), 3.687 (d, 1H, $J_{gem} = 14.6$ Hz, COCH_2Cl), 1.348 (d, 3H, $J_{6,5} = 6.2$ Hz, H-4^A), 1.313 (d, 3H, $J_{6,5} = 6.2$ Hz, H-4^C), 1.204 (d, 6H, $J_{6,5} = 6.2$ Hz, H-4^B, H-4^D); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1 (1C, *C*OCH$_2$Cl), 165.3–164.6 (7C, *C*OPh), 133.7–127.5 (C–Ar), 101.3 (C-1^B), 98.9 (2C, C-1^C, C-1^D), 97.4 (1C, C-1^A), 78.7 (1C, C-2^A), 75.9 (1C, C-2^B), 75.6 (1C, C-4^A), 74.6 (1C, C-3^C), 72.7 (1C, C-4^C), 71.5 (1C, C-4^B), 71.4 (1C, C-4^C), 71.1 (1C, C-4^D), 70.4 (1C, C-3^B), 70.3 (1C, C-3^D), 70.1 (2C, C-5^A, C-5^D), 69.5 (1C, C-2^D), 69.0 (1C, O*C*H$_2$Ph), 67.4 (2C, C-5^B, C-5^C), 66.2 (1C, C-3^A), 40.0 (1C, CO*C*H$_2$Cl), 18.8 (1C, C-6^A), 18.6 (1C, C-6^C), 18.5 (2C, C-6^B, C-6^D). ESI-MS for $C_{85}H_{81}ClO_{25}$ (*m*/*z*): M_r (calcd) 1496.4, M_r (found) 1519.3 $(M+Na)^+$. Anal. calcd: C, 65.75; H, 5.18. Found: C, 65.90; H, 5.18.

3.9. Benzyl (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-(3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1 → 3)]-4-*O*-benzoyl-α-L-rhamnopyranoside (13)

A suspension of acceptor **12** (100 mg, 0.067 mmol), imidate **3**[8] (81 mg, 0.134 mmol) and freshly powdered 4 Å molecular sieves in absolute dichloromethane (2 mL) was stirred at −10 °C. After 30 min TMSOTf (0.47 μL, 2.7 μmol) was added and the mixture was kept at −10 °C until TLC (2:1 cyclohexane–ethyl acetate) showed that **3** was completely consumed (3 h). The reaction was quenched with Et_3N (18 μL), the mixture was filtered over Celite, extracted with water, and dried. Silica gel chromatography (9:2 cyclohexane–ethyl acetate) gave two fractions, one affording unreacted acceptor **12** (52 mg, 51%), the other contained the desired pentasaccharide **13** (59 mg, 45%) as a white foam: $[\alpha]_D$ +53.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 8.18–7.24 (m, 40H, 8Ph), 5.812 (dd, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 3.2$ Hz, 1H, H-3^B), 5.644 (br s, 1H, H-2^C), 5.619 (t, $J_{4,3} = J_{4,5} = 10.0$ Hz, 1H-4^C), 5.594 (t, $J_{4,3} = J_{4,5} = 9.9$ Hz, 1H, H-4^B), 5.522 (br s, 1H, H-1^C), 5.467 (dd, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 3.2$ Hz, 1H, H-3^D), 5.419 (br s, 1H, H-1^B), 5.376 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^A), 5.321 (t, $J_{4,3} = J_{4,5} = 9.8$ Hz, 1H, H-4^D), 5.211 (br s, 2H, H-1^D, H-2^D), 5.114 (t, $J_{3,4} = J_{3,2} = 9.5$ Hz, 1H, H-3^E), 4.96–4.88 (m, 2H, H-1^A, H-4^E), 4.80–4.73 (m, 3H, H-1^E, NH, OCH_2Ph), 4.663 (dd, $J_{3,4} = 10.0$ Hz, $J_{3,2} = 3.3$ Hz, 1H, H-3^C), 4.599 (d, 1H, $J_{gem} = 12.0$ Hz), 4.585 (br s, 1H, H-2^B), 4.338 (dq, 1H, $J_{5,4} = 10.0$ Hz, $J_{5,6} = 6.2$ Hz, 1H, H-5^C), 4.31–4.07 (m, 8H, H-2^A, H-3^A, H-5^B, H-5^D, 2 × H-6^E, 2 × OCH_2CCl$_3$), 3.983 (dq, 1H, $J_{5,4} = 9.8$ Hz, $J_{5,6} = 6.2$ Hz, 1H, H-5^A), 3.745 (d, $J_{gem} = 15.0$ Hz, 1H, COCH_2Cl), 3.698 (d, $J_{gem} = 15.0$ Hz, 1H, COCH_2Cl), 3.654 (m, 1H, H-5^E), 3.523 (q, $J_{2,1} = J_{2,3} = 9.4$ Hz, 1H, H-2^E), 2.02–1.92 (3s, 9H, 3 × Ac), 1.457 (d, $J_{6,5} = 6.2$ Hz, 1H, H-6^D), 1.295 (d, $J_{6,5} = 6.2$ Hz, 1H, H-6^A), 1.256 (d, $J_{6,5} = 6.2$ Hz, 1H, H-6^B), 1.148 (d, $J_{6,5} = 6.2$ Hz, 1H, H-6^C); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1 (1C, *C*OCH$_2$Cl), 165.3–164.6 (8C, *C*OPh, *C*OCH$_2$CCl$_3$), 133.8–127.5 (C–Ar), 101.8 (C-1^E, $^1J_{C,H} = 164$ Hz), 100.5 (C-1^B), 99.3 (C-1^C), 99.0 (C-1^D), 98.1 (C-1^A), 95.3 (OCH$_2$*C*Cl$_3$), 78.5 (C-2^B), 78.1 (C-2^A), 77.0 (C-3^A), 74.7 (C-3^C), 73.8 (O*C*H$_2$CCl$_3$), 73.3 (C-4^A, C-4^C), 72.2 (C-2^C), 72.0 (C-4^B), 71.6 (C-5^E), 71.5 (C-4^D), 71.0 (C-3^E), 70.5 (C-3^D), 70.4 (C-3^B), 69.9 (C-2^D), 69.3 (O*C*H$_2$Ph), 69.0 (C-4^E), 67.6 (C-5^C), 67.3 (C-5^D), 67.2 (C-5^B), 66.9 (C-5^A), 62.3 (C-6^E), 56.1 (C-2^E), 40.2 (CO*C*H$_2$Cl), 21.0 (Ac), 18.1 (C-6^C), 17.5 (C-6^A, C-6^B), 17.3 (C-6^D). ESI-MS for $C_{85}H_{81}ClO_{25}$ (*m*/*z*): M_r (calcd) 1957.5, M_r (found) 1958.65 $(M+H)^+$. Anal. calcd: C, 59.42; H, 4.88; N, 0.71. Found: C, 59.49; H, 4.80; N, 0.70.

3.10. Benzyl α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl)-(1 → 2)-[2-deoxy-2-acetamido-β-D-glucopyranosyl-(1 → 3)]-α-L-rhamnopyranoside (1)

To a solution of **13** (39 mg, 0.020 mmol) in THF (4.0 mL) was added 2 M aqueous KOH (400 μL) and the mixture was stirred at 40 °C. After 19 h the TLC (5:1 isopropanol–water) showed that the reaction was complete. The mixture was diluted with MeOH (10 mL), neutralized with Amberlyst-15 H^+, filtered and dried. The residue was dissolved in methanol (3.0 mL) and Ac_2O (300 μL) was added. After 2 h the solution was dried to obtain and the residue was purified by gel filtration on a P-2 (Biorad) column using water as eluant, to obtain **1** (10 mg, 56%) as a white foamy solid: $[\alpha]_D$ −45 (*c* 0.5, H_2O); ^1H NMR (400 MHz, D_2O) (see also Table 1): δ 7.47–7.42 (m, 5H, Ph), 4.775 (d, 1H, $J_{gem} = 12.0$ Hz, OCH_2Ph), 4.629 (d, 1H, $J_{gem} = 12.0$ Hz, OCH_2Ph), 2.05 (s, 3H, Ac); ^{13}C NMR (100 MHz, D_2O)

(see also Table 1): δ 129.3 (Ar), 70.4 (OCH_2Ph), 21.1 (Ac). ESI-MS for $C_{39}H_{61}NO_{22}$ (m/z): M_r (calcd) 895.4, M_r (found) 918.4 $(M+Na)^+$. Anal. calcd: C, 52.28; H, 6.86; N, 1.56. Found: C, 52.45; H, 6.80; N, 1.55.

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